Toxicity of NaF and uptake of F to willows

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Publication date:
2015

Document Version
Peer reviewed version

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Why this study?

F polluted site at Fredericia, Denmark.

The municipality asked if we knew anything about phytotoxicity of F

Trees are lovely. Can't we make a park and remediate at the same time?

Scopes of the study

- Examine the toxicity and uptake of fluoride to willows, when they are exposed through their roots? (lab. study)

- Mass balance model for prediction of F uptake to willows

- Evaluate potential of phytoremediation at Fredericia

The willow tree toxicity test

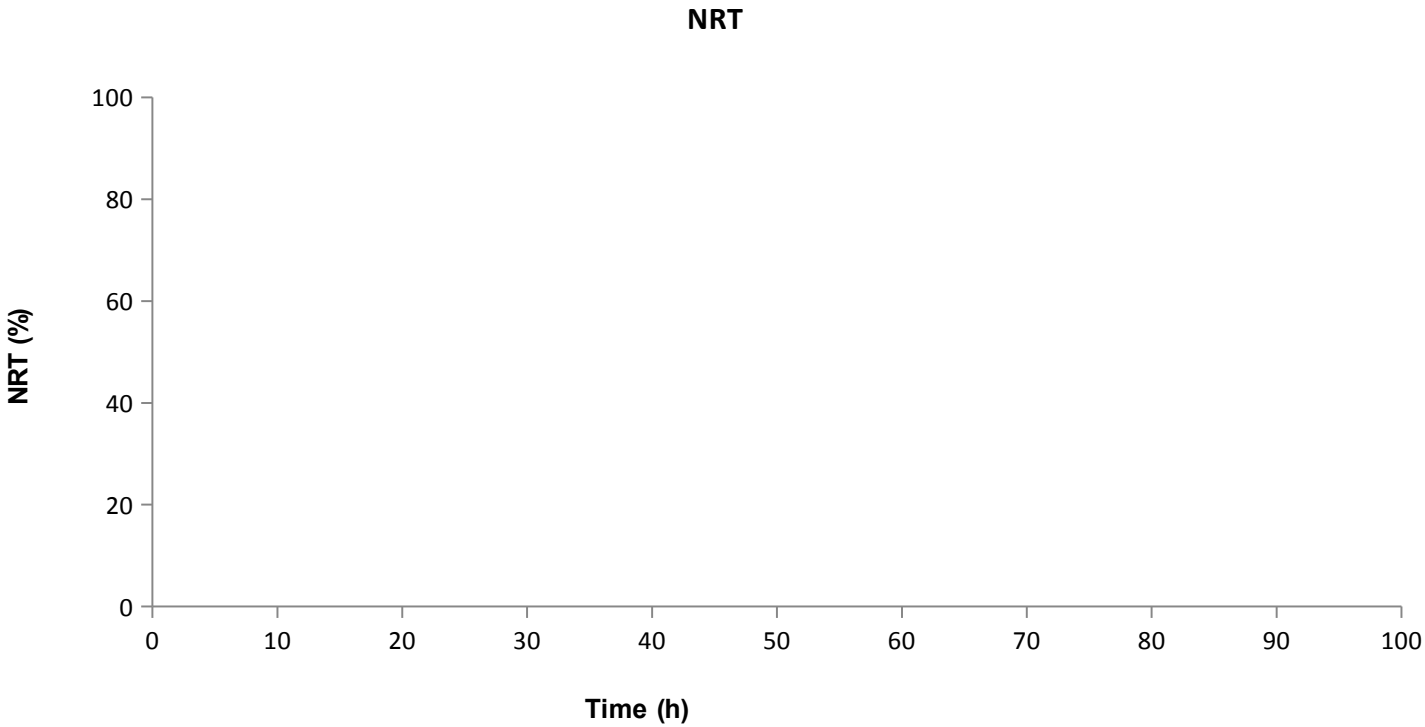
The philosophy: *"Healthy tree transpire more than weak trees"* (S. Trapp)

Normalized **R**alative **T**ranspiration (NRT)

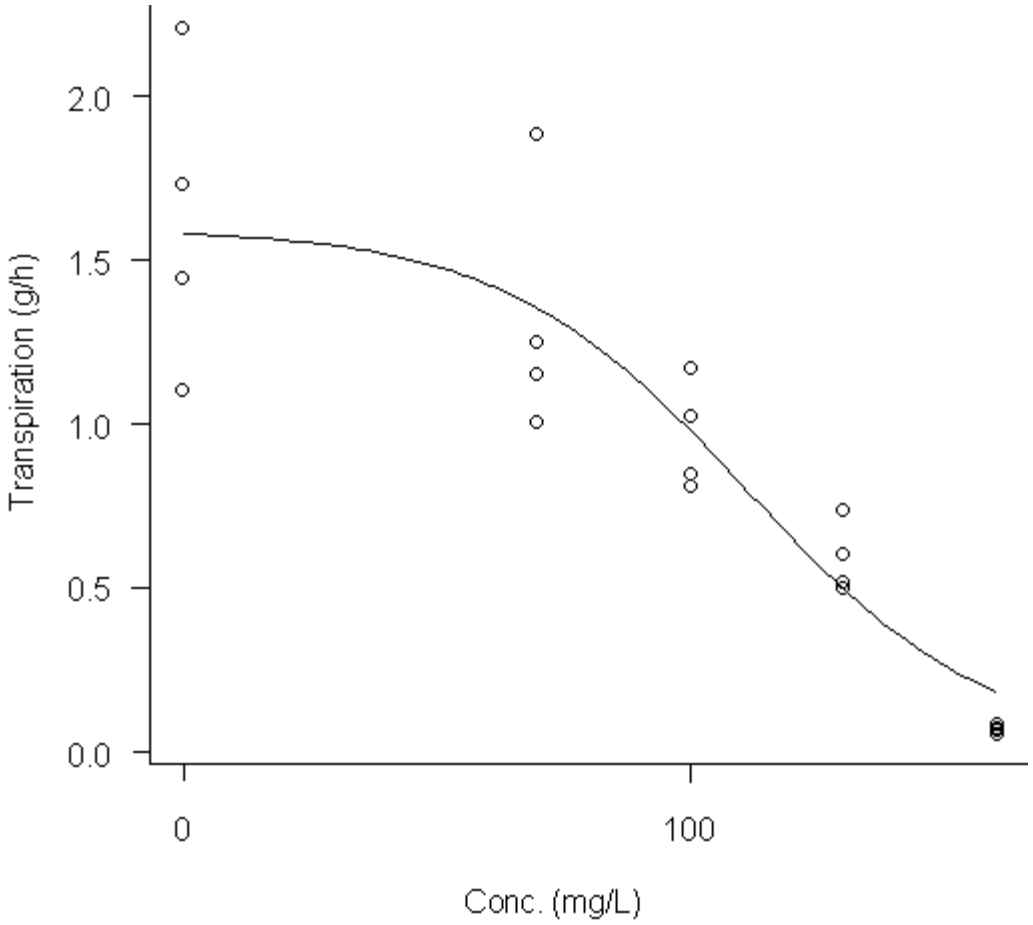
$$NRT(C,t)\ (\%) = \frac{\frac{1}{n}\cdot\sum_{i=1}^{n} T_i(C,t)/T_i(C,0)}{\frac{1}{m}\cdot\sum_{j=1}^{m} T_j(0,t)/T_j(0,0)}\times 100$$

The definitive test

pH	Before	After
Control	6.7	7.0
400 mg F/L	5.9	6.3



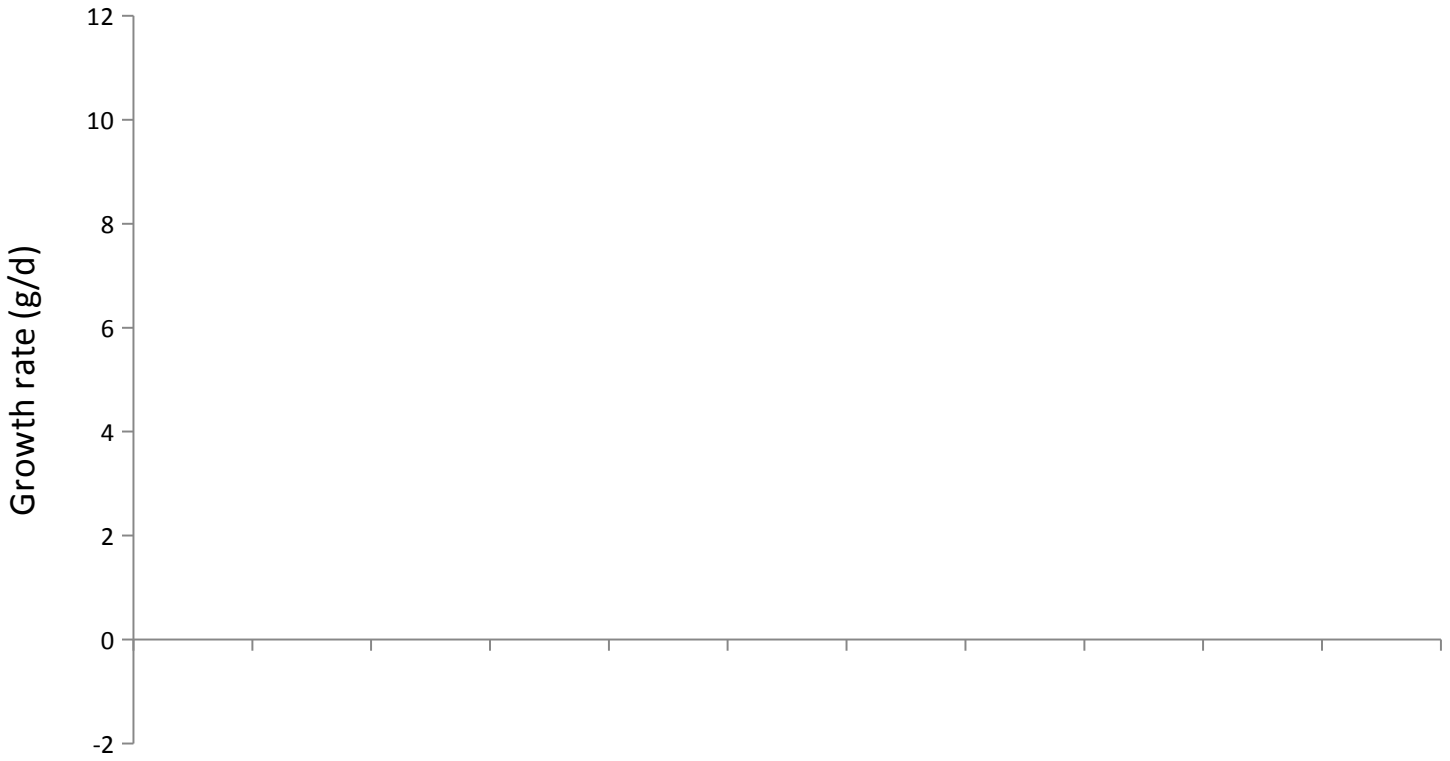
Calculating effect concentrations by R



EC_X	Estimate	95 % CI
EC_{10}	38.0	± 34.2
EC_{20}	59.6	± 40.7
EC_{50}	128.7	± 51.1

Log-logistic model fit with lower transp. boundary of 0 g/h

Average growth rates with 95% CI



Mass balance calculations

Conc. (mg/L)	Control	50	100	200	400
m_{Init} (mg)	0.0	20.9	42.2	84.6	162.8
m_{End} (mg)	0.1	21.0	41.6	83.5	159.7
m_{Loss} (mg)	-0.1	-0.1	0.6	1.1	3.1
C_p (mg/kg)	-1.4	-1.4	13.1	25.8	195.1
TSCF	-0.0	0.0	0.1	0.2	0.8

$$m_{init.,sol.} + m_{init.,tree} \rightleftharpoons m_{end,sol.} + m_{end,tree}$$

$$TSCF = \frac{Concentration\ in\ transpiration\ stream}{Concentration\ in\ external\ solution}$$

Modelling the uptake of fluoride

The model was used by Trapp et al. (2008) to describe uptake of slat to willows. It is basically just a mass balance.

Michaelis-Menten equation

$$v = \frac{v_{max} C_W}{K_M + C_W} M_R$$

The model assumes:

- That fluoride is taken up passively with the transpiration stream.

- Steady state.

- That the processes responsible for pumping out fluoride from the roots follows the Michaelis-Menten equation for enzymatic removal.

where v is the is the removal (mg/d), vmax is the maximal removal (mg/(kg plant and d)), C_W is the concentration in the external solution (mg/L), KM is the half-saturation constant, MR is the mass of the roots (kg), Q is the transp. (L/d), K_{RW} is the partitioning coefficient between root and water, k_R is the growth rate of the roots (1/d) and C_R is the conc. in the roots (mg/kg)

$$0 = \frac{K_M Q C_W}{M_R} + \frac{Q C_W C_R}{M_R} - \frac{K_M Q C_R}{M_R K_{RW}} - \frac{C^2{}_R Q}{M_R K_{RW}} - K_M k_R C_R - k_R C^2{}_R - v_{max} C_R$$

Solving this for C_R gives…

… A quadratic equation of the general form: $aC^2 + bC + C = 0$

With two solutions $C_R = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a}$

However only one realistic solution

where $a = -k_R \frac{Q}{M_R K_{RW}}$,

$b = \frac{C_W Q}{M_R} - \frac{K_M Q}{M_R K_{RW}} - k_R K_M - v_{max}$ and $c = \frac{C_W K_M Q}{M_R}$

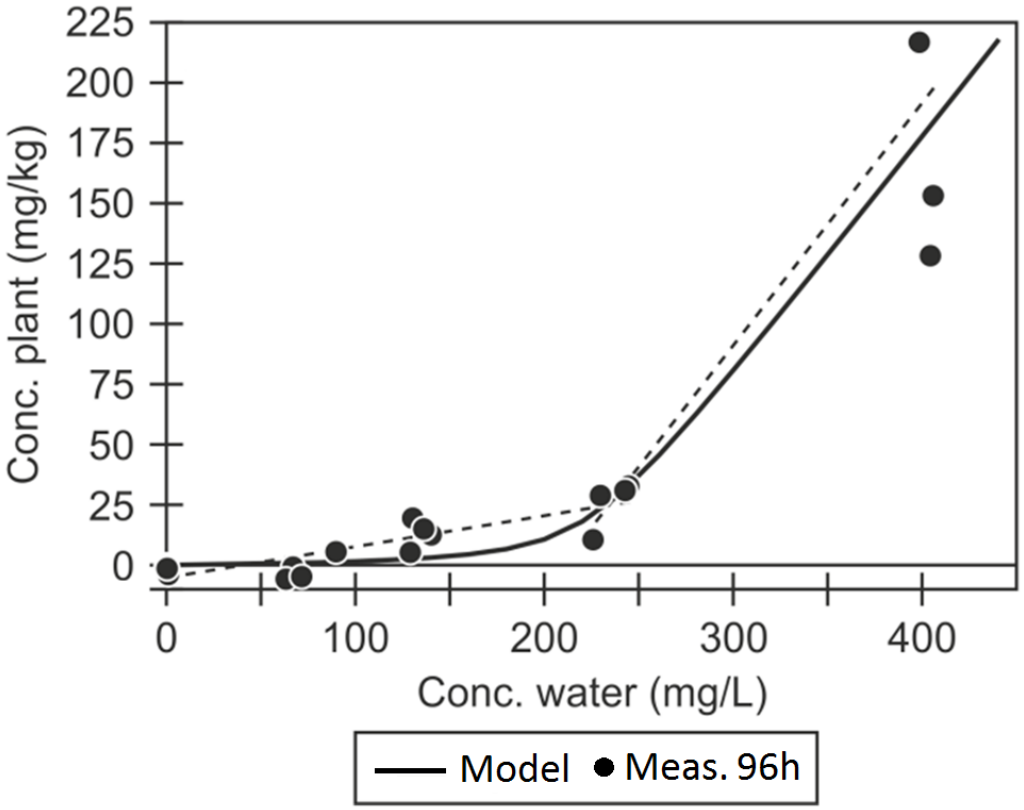
where vmax is the maximal removal (mg/(kg plant and d)), C_W is the concentration in the external solution (mg/L), KM is the half-saturation constant, MR is the mass of the roots (kg), Q is the transp. (L/d), K_{RW} is the partitioning coefficient between root and water, k_R is the growth rate of the roots (1/d) and C_R is the conc. in the roots (mg/kg)

Model results

$$v_{max} = C_{W0}\frac{Q}{M_R} = 8.992\ g/kg/d$$

On molar basis = 0.5 mole/(kg d)
The same obtained by Trapp et al. (2008) for salt

Break through point = 209.5 mg/L



Parameter	Value	Unit	Origin
Concentration in solution, C_W	0-400	mg/L	Measured
Root mass, m_R	0.001	kg	Estimated
Transpiration stream, Q	0.04	L/d	Measured average
Half-saturation constant, K_M	2	g/L	Fitted
Maximum enzymatic removal rate, v_{max}	8.992	g/kg/d	Fitted
Root growth rate, k_R	0	d^{-1}	Estimated

	Equation	Valid conc.	R^2	n	P
Regression 1	y = 0.128x – 5.186	C < 209.5 mg/L	0.764	16	<<0.001
Regression 2	y = 1.005x – 210.5	C > 209.5 mg/L	0.790	8	< 0.005

Potential for phytoremediation

Assuming:

A = 1 ha, pollution depth = 2 m, C_{soil} = 200 mg F/kg, soil density = 2 kg/L, 100 L of water in order to produce 1 kg of plant (Larcher, 2003), C_{water} 50 mg F/L and a production of plant mass per square meter per year of 2 kg .

Total mass of fluoride = 8000 kg.

TSCF at 50 mg F/L is approximately 0.1.

Total removal time is then approximately 800 years.

Conclusions

- The phytotoxicity of fluoride has been assessed through the willow tree toxicity test. EC10: 38.0±34.2 EC20: 59.6±40.7 and EC50:128.7±51.1 (mg F/l)
- Uptake of fluoride to willows could be described by a non-linear mathematical mass balance model indicating a break through point at 209.5 mg F/L and with a maximum enzymatic removal rate of 8992 mg/kg/d
- The mechanisms responsible for pumping out F from plant cells are most likely the same responsible for pumping Cl out
- Phytoremediation at Fredericia takes approx. 800 years

?

Questions

Transpiration of the controls

Table 5.2: Transpiration rates (g/h) of the control trees during the different time intervals of the preliminary willow tree toxicity test.

Category	Tree no.	0-16,75h	16,75-41h	41-72h	72-92,5h
Control	3	1,654	1,674	1,594	1,634
Control	6	1,200	1,225	1,181	1,210
Control	13	0,985	0,990	0,942	0,922
Control	16	0,991	1,035	1,065	1,132
Control	20	1,313	1,344	1,319	1,346

C_{end}/C_{Init}

Table 5.3: Ratios of fluoride concentration in external solution before and after the preliminary and definitive test (C_{End}/C_{Init}). Concentrations were measured by conductivity meter.

Conc. (mg F/L)	**1**	**10**	**50**	**100**	**200**	**400**	**1000**
Preliminary test	1.56	1.24	-	1.21	-	-	0.99
Definitive test	-	-	1.46	1.35	1.18	1.01	-

pH and dissociation

$$\alpha_{non-dissociated\ acid} = \frac{1}{1+10^{(pH-pKa)}}$$

where pK_a is the acid dissociation constant.

pK_a (HF) = 3.17 ➔ 0.1 % non-dissociated HF at pH 6.
app. 1 % non-dissociated HF at pH 5.